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Electronic Supplementary Information (13 pages)

1. Materials and methods

2. Synthetic route to pillar[5]arene H


4. X-ray crystal data of H⇒G1

5. Electrospray ionization mass spectrometry of an equimolar solution of H and G1

6. NOESY NMR analysis of H⇒G1

7. A photo showing color changes after host–guest complexation

8. Fluorescence titration experiments of H, G1 and G2 in acetonitrile


10. Electrospray ionization mass spectrometry of an equimolar solution of H and G2

11. Determination of association constants of complexes H⇒G1 in acetonitrile

12. 1H NMR titration of H with G2

13. Job plots of H⇒G1 based on UV-vis spectroscopy data in acetonitrile

14. Partial 1H NMR spectra
1. Materials and methods

Pillar[5]arene $\text{H}^\text{S1}$ and guest $\text{G1}^\text{S2}$ were synthesized according to the literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. $^1\text{H}$ NMR spectra were collected on a temperature-controlled 400 MHz spectrometer. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. The crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structures were solved by SHELXS-97 and refined by SHELXL-97. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).
2. Synthetic route to pillar[5]arene H

![Scheme S1 Synthetic route to pillar[5]arene H.](image)


*per*-Hydroxylated pillar[5]arene (0.42 g, 0.68 mmol) was dissolved in CH$_3$CN (50 mL). K$_2$CO$_3$ (2.25 g, 16.30 mmol) was added and the reaction mixture was stirred. Then 2-methoxyethyl $p$-toluenesulfonate (4.10 g, 21.30 mmol) was added and the reaction mixture was stirred under N$_2$ at reflux for 5 days. The solvent was evaporated and the residue was dissolved in CH$_2$Cl$_2$. The resultant solution was washed with H$_2$O and brine. The organic phase was collected, dried over anhydrous Na$_2$SO$_4$ and concentrated to give a crude solid. Column chromatography (silica gel; CH$_2$Cl$_2$:CH$_3$OH =50:1) afforded a light yellow solid (150 mg, 18.46%). The $^1$H NMR spectrum of pillar[5]arene H is shown in Figure S1. $^1$H NMR (400 MHz, CD$_3$CN, room temperature) $\delta$ (ppm): 6.96 (10 H, s), 4.00 (20 H, s), 3.74 (20 H, d, $J = 4.2$ Hz), 3.72 (10 H, s), 3.38 (30 H, s).
3.23

Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, room temperature) of pillar[5]arene H.

4. X-ray crystal data of H·G1

Crystal data of H·G1: red, C₁₆₈H₂₁₇F₂₄O₄₀N₇P₄, FW 3554.37, triclinic, space group P-1, a = 12.6852(6), b = 17.3581(6), c = 21.7669(9) Å, α = 104.590(3)°, β = 100.420(4)°, γ = 95.616(3)°, V = 4509.7(3) Å³, Z = 1, Dc = 1.309 g cm⁻³, T = 170 K, μ = 0.141 mm⁻¹, 11015 measured reflections, 18372 independent reflections, 384 parameters, 3 restraints, F(000) = 1870.0, R₁ = 0.1206, wR₂ = 0.0708 (all data), R₁ = 0.2313, wR₂ = 0.1904 [I > 2σ(I)], max. residual density 1.309 e·Å⁻³, and goodness-of-fit (F²) = 1.042. CCDC-1001509.

5. Electrospray ionization mass spectrometry of an equimolar solution of H and G1

Fig. S2 Electrospray ionization mass spectrometry of an equimolar solution of H and G1.
6. NOESY NMR analysis of $\text{H} \supset \text{G1}$

![NOESY NMR analysis](image)

**Fig. S3** Partial NOESY NMR analysis of $\text{H} \supset \text{G1}$ (3.00 mM) in CD$_3$CN with a mixing time of 800 ms (500 MHz, 298 K).

7. A photo showing color changes after host–guest complexation

![Color changes](image)

**Fig. S4** A photo showing color changes after host–guest complexation in acetonitrile: (a) $\text{H}$ alone; (b) an equimolar solution of $\text{H}$ and $\text{G1}$; (c) $\text{G1}$ alone;
8. Fluorescence titration experiments of H, G1 and G2 in acetonitrile

To determine the stoichiometry and association constant for the complexation between H and G1 (or G2), fluorescence titration experiments were done with solutions which had a constant concentration of H (1.00 \( \times \) 10\(^{-5} \) M) and varying concentrations of G1 (or G2). By a non-linear curve-fitting method, the association constant \((K_a)\) of \(\text{H} \rightleftharpoons \text{G1}\) or \(\text{H} \rightleftharpoons \text{G2}\) was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexations between H and G1, and between H and G2.

The non-linear curve-fittings were based on the equation:

\[
\Delta F = \left( \frac{\Delta F_\infty}{[\text{H}]_0} \right) (0.5[\text{G}]_0 + 0.5([\text{H}]_0 + 1/K_a) - (0.5 ([\text{G}]_0^2 + (2[\text{G}]_0 (1/K_a - [\text{H}]_0)) + (1/K_a + [\text{H}]_0)^2)^{0.5})
\]

Where \(\Delta F\) is the fluorescence intensity changes at 326 nm at \([\text{G}]_0\), \(\Delta F_\infty\) is the fluorescence intensity changes at 294 nm when H is completely complexed, \([\text{G}]_0\) is the initial concentration of G1 (or G2), and \([\text{H}]_0\) is the fixed initial concentration of H.

![Fluorescence spectra of H](image)

**Fig. S5** Fluorescence spectra of H at a concentration of 1.00 \( \times \) 10\(^{-5} \) M in acetonitrile solution at room temperature with different concentrations of G1: 0, 0.249, 0.498, 0.744, 0.990, 1.23, 1.48, 1.72, 1.96, 2.44, 3.38, 6.10 and 10.3 \( \times \) 10\(^{-5} \) M in acetonitrile solution.
**Fig. S6** Mole ratio plot for H and G1, showing a 1:1 complexation stoichiometry.

**Fig. S7** The fluorescence intensity changes of H upon addition of G1. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.
Fig. S8 Fluorescence spectra of H at a concentration of $1.00 \times 10^{-5}$ M in acetonitrile solution at room temperature with different concentrations of G2: 0, 0.249, 0.498, 0.744, 0.990, 1.23, 1.48, 1.72, 1.96, 2.44, 3.38, 6.10 and $10.3 \times 10^{-5}$ M in acetonitrile solution.

Fig. S9 Mole ratio plot for H and G2, showing a 1:1 complexation stoichiometry.
Fig. S10 The fluorescence intensity changes of H upon addition of G2. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.


Fig. S11 Partial ¹H NMR spectra (400 MHz, CD₃CN, 25 °C): (a) 1.00 mM H; (b) 1.00 mM H and G2; (c) 1.00 mM G2.
10. Electro spray ionization mass spectrometry of an equimolar solution of $H$ and $G_2$

![Fig. S12](image-url) Electro spray ionization mass spectrometry of an equimolar solution of $H$ and $G_2$.

11. Determination of association constants of complexes $H\supseteq G_1$ in acetonitrile

The association constants (Ka) of complexes $H\supseteq G_1$ were determined by probing the charge-transfer band of the complexes by UV-vis spectroscopy and employing a titration method. Progressive addition of an acetonitrile solution with high guest concentration and low host concentration to an acetonitrile solution with the same host concentration resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the association constants (Ka): $5.0 \pm 0.8 \times 10^4 \text{ M}^{-1}$
Fig. S13 (a) The absorption spectral changes of H (0.05 mM) upon addition of G1 and (b) the absorbance intensity changes at $\lambda = 560$ nm upon addition of G1 (from 0 to 1.7 mM). The red solid line was obtained from the non-linear curve-fitting.

12. $^1$H NMR titration of H with G2

$^1$H NMR titration was done with solutions which had a constant concentration of G2 (1.00 mM) and varying concentrations of H. By a non-linear curve-fitting method, the association constant between the guest G2 and host H was calculated.

Fig. S14 $^1$H NMR spectra (acetonitrile-$d_3$) of G2 at a concentration of 1.0 mM with different concentrations of H.
**Fig. S15** The chemical shift changes of H on G2 upon addition of H. The red solid line was obtained from the non-linear curve-fitting.

13. **Job plots of H=G1 based on UV-vis spectroscopy data in acetonitrile**

**Fig. S16** Job plots showing the 1:1 stoichiometries of the complexes between H and G1 in acetonitrile.([H]+[G1]=2.00 Mm)
14. Partial $^1H$ NMR spectra

Fig. S17 Partial $^1H$ NMR spectra (400 MHz, CD$_3$CN, 25 °C): (a) 1.00 mM G2; (b) 1.00 mM G1; (c) 0.500 mM H, G2 and G1; (d) 0.500 mM H and G2; (e) 1.00 mM H.

References:

